Polymer Bulletin 5, 19–24 (1981)

Polymer Bulletin

Syntheses of Block Copolymers of 2-Methyl-2-oxazoline and Aromatic Vinyl Compounds

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SUMMARY

Various polymers of aromatic vinyl compounds having haloalkyl groups at the both chain-ends were prepared by terminating the living anionic polymers with 1,2-dichloroethane or 1,4-dibromobutane. Using these polymers as initiators, 2-methyl-2-oxazoline was polymerized to result in the block copolymers.

INTRODUCTION

Alkyl halides are known to initiate the ring opening polymerization of oxazolines (SAEGUSA et al 1972). Polymers containing haloalkyl groups, hence, are able to initiate the polymerization of oxazolines to yield block or graft copolymers. The graft copolymerization of 2-methyl-2-oxazoline (MeOZO) onto chloromethylated polystyrene was reported by SAEGUSA et al (1975). More recently SEUNG et al (1979a, 1979b, 1980) obtained the block copolymers of MeOZO by using the polymers having iodines at the chain-end as initiators. They prepared these "initiator polymers" by polymerizing styrene, styrene oxide, and isobutyl vinyl ether with iodine as an initiator. Such "initiator polymers",however,do not always contain quantitative amount of iodine at every chain end. In addition to this disadvantage, the kind of monomers which can be used in this method is limited in number, and the molecular weight of the polymers resulted from the initiation with iodine is always low.

We prepared various polymers of aromatic vinyl compounds having haloalkyl groups at the both chain-ends by anionic polymerization followed by terminating the living anion with an excess of α,ω-dihaloalkane. Using these polymers as initiators, we are successful in preparing ABA triblocks of MeOZO. Some of the advantages of this method are as follows: (1) all monomers susceptible to anionic living polymerization can be utilized as the source of one block segment, (2) the control of the degree of polymerization of a block sequence can easily be achieved, and (3) since the selection of the initiator for the anionic polymerization gives polymers having haloalkyl groups either at one end or both ends, AB diblock or ABA triblock copolymer can be prepared at one's choice.

EXPERIMENTAL

0170-0839/81/0005/0019/$01.20

Materials

Styrene was distilled twice under reduced pressure onto calcium hydride followed by distillation onto a freshly-formed sodium mirror. 2-Vinylnaphthalene (VNp) purchased from Aldrich Co. was purified by sublimation twice and then dried on calcium hydride under high vacuum overnight. 9-Vinylphenanthrene (VPh) was prepared from phenanthrene-9--carboxyaldehyde by the Wittig reaction (MÄRKL et al 1973), purified on a silica-gel column using n-hexane as an eluent, and recrystallized from n-hexane. 1,2-Dichloroethane and 1,4-dibromobutane were distilled twice from phosphorus pentoxide onto calcium hydride, and freshly distilled on a vacuum line immediately before use. MeOZO purchased from Aldrich Co. was distilled under nitrogen and dried with molecular sieves. Dimethylformamide (DMF) was dried with potassium hydroxide and distilled under reduced pressure in the presence of p-toluenesulfonic acid. Other reagents and solvents were purified by usual methods.

Anionic Polymerization

Anionic polymerizations were carried out in a glass apparatus equipped with break-seals on a high vacuum line at 0°C for 1 hr in accordance with usual procedures using sodium naphthalene as an intiator and tetrahydrofuran (THF) as a solvent.

Reaction of the Living Polymer with α,ω-Dihaloalkane

An ampoule fitted with a breakable capillary seal containing a THF solution of the living polymer was connected to a reaction flask which contained an excess of 1,2-dichloroethane (or 1,4-dibromobutane) in a THF solution. The whole system was thoroughly evacuated on the vacuum line and sealed off. The living polymer solution was then added onto the dihaloalkane solution dropwise by breaking the capillary seal. A small amount of the living polymer solution was saved in a sampling tube branched from the main ampoule for a GPC measurement. This "killing" reaction was continued at 0°C for 1 hr under stirring. The polymers thus obtained were purified by three reprecipitations from a THF solution into methanol and freeze-dried from the benzene solution.

Block Copolymerization

In order to accomplish the initiation efficiency as high as possible, special precaution was taken for the purification of the materials. A representative example of the block copolymerization is as follows: A 10-ml solution of benzene containing 0.70 g of polyVNp was placed in an ampoule containing 0.20 g of potassium iodide and then benzene was thoroughly removed by freeze-drying technique. Into the ampoule were distilled 5 ml of DMF and 5.5 g of MeOZO, successively, on a vacuum line. After sealing off the ampoule, it was placed in an oil bath termostatted at 140°C for 24 hr to carry out the polymerization. The ampoule was then opened, 100 ml of chloroform was added to the mixture, and the polymer was reprecipitated into 500 ml of n-hexane. The block copolymerizations of styrene and VPh were also carried out in a similar manner.

Fractionation

Fractionation

Total fractionation procedures are shown in Fig.1. The whole polymer thus obtained was first fractionated into methanol-soluble and insoluble parts by refluxing in methanol for 24 hr followed by centrifugation. The methanol-insoluble fraction was then divided into benzene-soluble part A and insoluble part B by extracting with benzene. The methanol-soluble fraction was also further fractionated into water-insoluble part C and soluble part D by refluxing in water containing small amount of methanol.

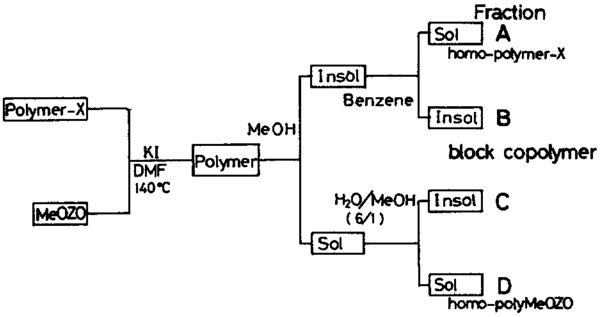
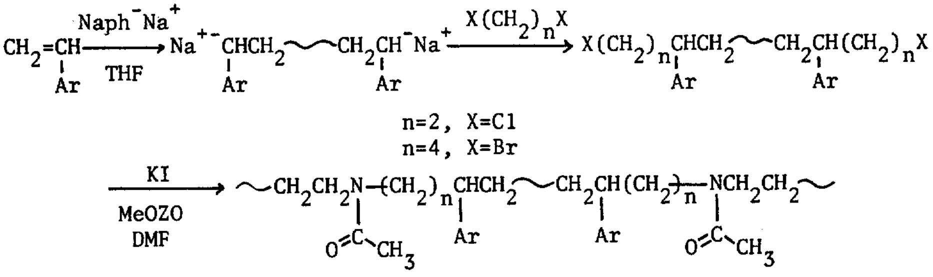


Fig.1. Fractionation of the block copolymers.

RESULTS AND DISCUSSION

The total schemes for the preparation of the block copolymers are as follows:



$$CH_2=\underset{Ar}{CH} \xrightarrow[THF]{Naph^-Na^+} Na^{+-}\underset{Ar}{CH}CH_2\sim\sim CH_2\underset{Ar}{CH}^-Na^+ \xrightarrow{X(CH_2)_nX} X(CH_2)_n\underset{Ar}{CH}CH_2\sim\sim CH_2\underset{Ar}{CH}(CH_2)_nX$$

n=2, X=Cl

n=4, X=Br

$$\xrightarrow[MeOZO\ DMF]{KI} \sim CH_2CH_2\underset{O=C-CH_3}{N}-(CH_2)_n\underset{Ar}{CH}CH_2\sim CH_2\underset{Ar}{CH}(CH_2)_n-\underset{O=C-CH_3}{N}CH_2CH_2\sim$$

Ar= Phenyl, naphthyl, phenanthryl

Fig.2 shows the GPC curve for polystyrene containing bromine at the chain-ends obtained by killing the polystyryl living anion with 1,4-dibromobutane. Little or no difference in the molecular weight and its distribution was found between before and after killing, which suggests that the addition of the living polymer solution dropwise onto a large excess of the dihaloalkane solution prevents the inter-chain-ends reaction of the living polymer with the dihaloalkane.

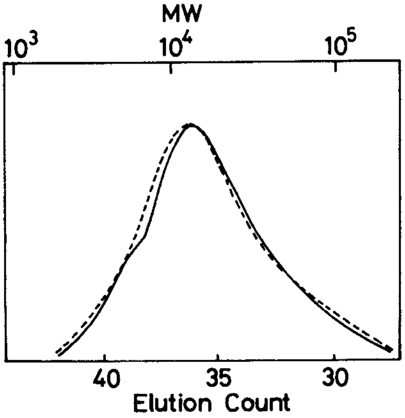


Fig.2. GPC elution curves for polystyrene before(----) and after(——) terminating with 1,4-dibromobutane.

The elemental analysis of the polymer assured that bromine was almost quantitatively introduced at the both chain-ends. The absence of the inter-molecular reaction was also confirmed in the same way for poly-VNp and polyVPh.

The solubility characteristics of the block copolymer of VNp and MeOZO are summarized in TABLE 1. All fractions are soluble in chloroform and DMF but insoluble in ether. The solubilities of the fraction A and D are identical with those of the initiator polymer and the homo-polyMeOZO, respectively. These solubility characteristics , combined with the NMR spectra of those fractions, led us to the idea that the fraction A is the homopolymer of initiator, B and C block copolymers, and D the homopolymer of MeOZO. The amount of each fraction is presented in weight in TABLE 2. Trace amounts of the initiator

TABLE 1. Solubility Characteristics of Poly(VNp-b-MeOZO)

Solvent	PolyVNp	PolyMeOZO	Poly(VNp-b-MeOZO),fraction			
			A	B	C	D
Water	I	S	I	I	I	S
Methanol	I	S	I	I	S	S
Ethanol	I	S	I	I	S	S
Ether	I	I	I	I	I	I
Benzene	S	I	S	I	I	I
THF	S	I	S	I	I	I
Chloroform	S	S	S	S	S	S
DMF	S	S	S	S	S	S

S, soluble; I, insoluble

TABLE 2. Block Copolymerization of MeOZO and Fractionation of the Resulting Polymers

Polymer(X)$^{a)}$	/g	MeOZO/g	Fraction/g A	B	C	D
Polystyrene(Br)	0.28 (0.26)	4.0	0	0.41 (0.48)	4.44	
PolyVNp(Cl)	0.70 (0.11)	5.5	0.08	0.11 (0.27)	2.13 (0.32)	3.88 (0.14)
PolyVPh(Cl)	0.50 (0.09)	5.0	0.02	0.61 (0.46)	0.81	2.81 (0.19)

a), Initiator polymer having halogen(X) at the chain-ends.
( ), Reduced viscosity (dl/g) of the chloroform solution (0.3 g/dl) at 30 °C.

homopolymer was found, whereas somewhat large quantity of homo-polyMeOZO was found to have been produced during the polymerization. In order to examine the formation of the latter homopolymer, the homopolymerization of MeOZO was carried out under the identical conditions with those for the block copolymerization except in the absence of the initiator polymer. However, no noticeable polymerization occurred. This led us to the conclusion that the homo-polyMeOZO was produced as a result of the chain transfer reaction during the block copolymerization. LITT et al (1975) studied the mechanism of the ring opening polymerization of oxazolines and suggested that the major site of the chain transfer is the carbon at the α-position to the 2-carbon of the ring. Accordingly, the formation of homo-polyMeOZO durng the block copolymerization seems to be inevitable to some extent. On the other hand, SEUNG et al (1979a,1979b,1980) did not touch upon the formation of the homo-polyMeOZO during the block copolymerization in their study. However, it seems to be reasonable to consider that the methanol-soluble fractions of their block copolymers are also contaminated with a significant amount of homo-polyMeOZO.

The reduced viscosities of the fractions are also shown in TABLE 2. The viscosities of the fraction B and C are both higher than those of the initiator polymer and the homo-polyMeOZO. These observations support the idea that the fraction B and C are the block copolymers.

The NMR spectrum for the fraction B of the block copolymer of VNp and MeOZO is shown in Fig.3. The assignments of each peak given in

TABLE 3. MeOZO Contents of the Block Copolymer Fraction B

Block Copolymer	MeOZO content, mol% NMR	UV	anal.$^{a)}$
Poly(St-b-MeOZO)	68.3	--	69.4
Poly(VNp-b-MeOZO)	72.5	--	71.8
Poly(VPh-b-MeOZO)	--	87.4	89.3

a), Calculated from the C/N ratio in the elemental analysis.

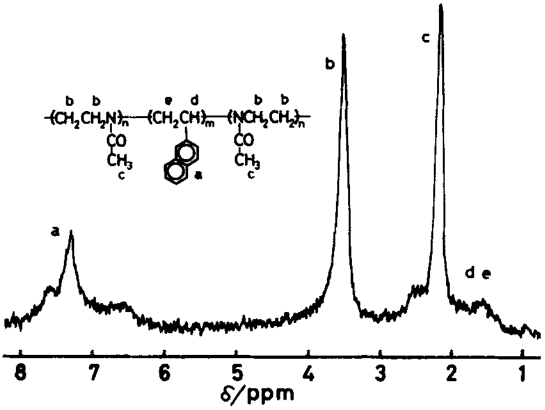


Fig.3. 100-MHz NMR spectra of poly(VNp-b-MeOZO) in $CDCl_3$ at room temperature.

Fig.3 assure that the block copolymer in fact contains the both monomeric units. For the block copolymer of VPh and MeOZO, the contents of MeOZO units in the fraction B were determined by UV spectra because the NMR spectra of this copolymer was too broad even at an elevated temperature (This is usually the case for polyVPh homopolymer). The contents determined by NMR or UV are in good agreement with those determined by elemental analyses (TABLE 3). From these contents, together with the GPC data, the block copolymer of VNp and MeOZO, for example, can roughly be regarded as an ABA triblock consisting of 25 units of VNp as a central sequence and 70 units of MeOZO as the side sequences.

Having succeeded in the syntheses of the block copolymers of MeOZO, our interest has been directed toward the derivation into the amphiphilic block copolymers consisting of cationic polyelectrolyte sequences from the block copolymers obtained in the present study. The reduction of the acetamide groups in the MeOZO segments and the subsequent quaternization are now under investigation.

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Received May 25, 1981
Accepted June 9, 1981